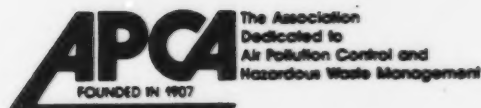


**SIMPLE TECHNIQUES FOR AT-SOURCE REDUCTION
OF WASTES FROM METAL FINISHING OPERATIONS**

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INTRODUCTION

Recently waste reduction at source has emerged as an issue because of increasingly stringent provincial regulations and municipal sewer-use bylaws. In Manitoba, for example, new provincial regulations have established a cradle-to-grave tracking system for the movement of all hazardous wastes. Waste generators are required, beginning in 1988, to provide detailed information on the nature and quantity of the waste generated, and to inform the Province of any major production changes. Failure to comply with the regulations can result in penalties, including fines not exceeding fifty thousand dollars or up to six months imprisonment. One can say that the time for waste reduction has come!

Generators of small quantities of hazardous waste are often not aware of the availability of waste reduction techniques. Furthermore, they often lack the capability to devise cost-effective waste management strategies.

A technical assistance program was initiated in the fall of 1986 by the Western and Northern Region of Environmental Protection, Environment Canada. It is directed at small industries, the first being metal finishing operations.

The program provides two major services in waste reduction: (1) field assessment and (2) training. In addition to the technical assistance program, Environment Canada also provides financial incentives in waste reduction.

This paper introduces the services of the technical assistance program and describes simple techniques that can be used for waste reduction at source in the metal finishing industry. A case study complements this presentation.

FIELD ASSESSMENT

The field assessment focuses on practical options for reducing waste generation at source. Comprehensive waste audits are carried out by a project team during visits to selected metal finishing shops. The steps used in the plant assessment process are illustrated in Figure 1.

The purposes of a field assessment are:

- . To identify sources of waste streams
- . To characterize waste streams quantitatively and qualitatively
- . To assess operational procedures
- . To identify raw material/chemicals used in plating processes

The results of the waste audit are then used to provide recommendations for waste management alternatives to disposal.

Two Manitoba metal finishing plants have been receiving technical assistance since December 1986. A two-phased strategy which will be described later has been recommended to improve their waste management practice. Two Alberta metal plating shops received field assessments in 1987.

It is to be expected that this program will also reveal what "source reduction techniques" mean in practice and how much these techniques can achieve.

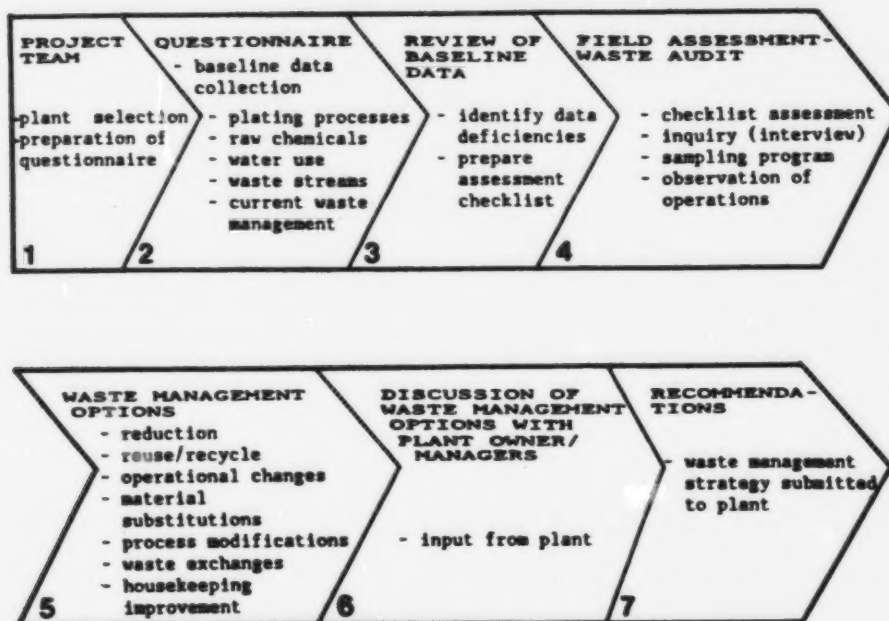


Figure 1 Plant assessment process

TRAINING

Environment Canada has developed a 3-part video-tape training course on metal finishing waste management. The first part is directed to plant owners/managers. The main objective of the first part is to assist them in understanding how to manage their wastes in a cost-effective way, and to make them aware of the value of training their employees.

Part one of the video-tape course deals with the following subjects:

- . Requirements for pollution prevention
- . Environment Canada guideline requirements
- . Waste generation pollution prevention
- . Pollution sources
- . Planning for pollution control
- . In-plant controls for pollution prevention

The video-tape presentation offers the advantage of being able to reach a large group of individuals at one time. The students' workbooks can be used by attendees for future reference. A video-tape presentation alone, however, can not be tailored to all regional specific needs. To address this shortcoming, we in the Western and Northern Region of Environment Canada incorporated other objectives that we wished to get across to plant owners/managers, first, to stress simple techniques for at-source waste reduction, and second, to make the planters aware of local regulatory requirements. The video-tape presentation was, therefore, supplemented with the following presentations and materials:

- . A case study presented by a waste treatment equipment supplier
- . Presentations on regulations by Alberta Environment and the cities of Edmonton and Calgary
- . Source reduction techniques
- . Information on two federal government financial incentive programs in waste reduction for pollution abatement
- . Presentation on the "On-Site" program for the temporary employment of technical staff to work on waste problems

The training session was held on November 17-19, 1987 in Edmonton, Alberta. It attracted 33 persons from all four western provinces of Canada.

FEDERAL GOVERNMENT FINANCIAL INCENTIVES

There are two federal government assisted financial incentive programs that may be applied to waste reduction, namely, the Development and Demonstration of Resource and Energy Conservation Technology (DRECT) and the Accelerated Capital Cost Allowance (ACCA).

Under DRECT, the federal government will pay up to 50% of the cost of developing and demonstrating prototype systems of promising new technologies that reduce pollution and save energy. ACCA is a tax incentive program. An

eligible taxpayer may write off the cost of capital equipment or processes installed for the prime aim of preventing and controlling air and water pollution over two years instead of the usual depreciation period.

SIMPLE TECHNIQUES FOR WASTE REDUCTION

For small plants, it is well recognized that a reliable end-of-pipe treatment and disposal system at reasonable capital and operation costs can only be realized if waste volume and its concentration of pollutants can be minimized at source. Thus, implementation of a waste management program at a metal finishing facility may be divided into two phases:

- . Phase I - at-source reduction of the volume and toxicity of wastes
- . Phase II - end-of-pipe treatment and disposal

Phase II should be considered as a last resort after every attempt has been made to reduce waste generation.

There are many simple techniques available for at-source reduction of the volume and toxicity of wastes. In this paper, simple techniques imply any measures which are technologically simple, low risk and low cost, or are not technologically simple but well understood by all platers. For the purpose of discussions, they are grouped into the following eight categories:

- . Reactive rinsing
- . Countercurrent rinsing
- . Dragout minimization
- . Dragout recovery (dragout tanks)
- . Process modifications/operational changes
- . Material substitutions
- . Waste exchange opportunities
- . Housekeeping improvement

Reactive Rinsing

Reactive rinsing is the reuse of rinsewater within a plating facility. This technique takes advantage of the nature of the contaminated rinse water to minimize water usage. Its applications in various finishing processes are illustrated in Figures 2 and 3. In contrast, Figure 4 is an example of misapplication of reactive rinsing; the pH of acid dip rinse can be as low as 2.5. Under pH 2.5-3.0, cyanide can be readily converted to hydrogen cyanide and evolved from the process.

Countercurrent Rinsing

In recent years, counterflow rinsing has gained prominence as a tool of conserving water and reducing the cost of waste water treatment. It also provides an opportunity to recycle rinse water to the plating tank to replenish evaporative losses.

In this system, clean water is added to the last rinse tank. The water overflows up the row of rinse tanks in a direction counter to the progress of the product. The amount of rinse water is a function of the maximum allowable concentration in the final rinse tank which will not interfere with the plating process.

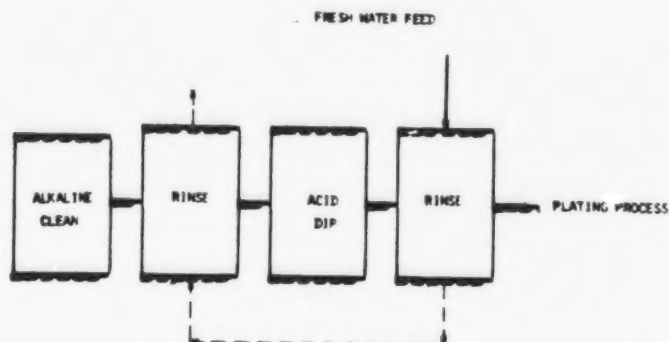


Figure 2 Basic cleaning process

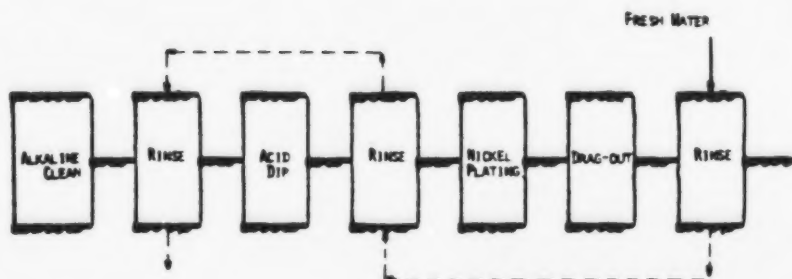


Figure 3 Example of reactive rinsing in a nickel plating process

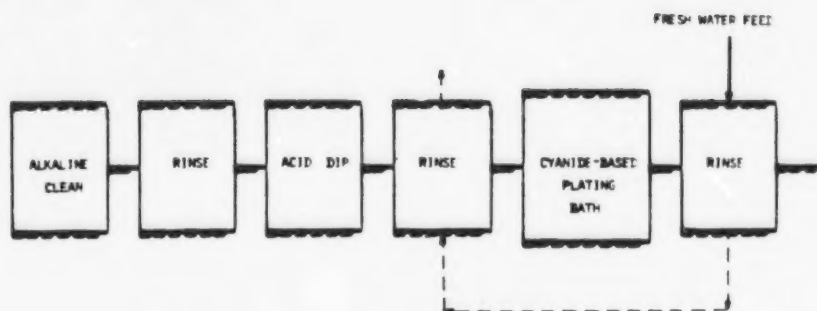


Figure 4 Dangerous misapplication of reactive rinsing

Complete Mixing. It should be noted that the success of counterflow rinsing depends on complete mixing of rinse water taking place in a rinse tank. To get better mixing:

- . Use agitation.
- . Introduce fresh water feed into the bottom of a rinse tank through a submerged perforated distribution pipe or diffuser.

The latter is of particular importance when using long, narrow rinse tanks.

Air Agitation. Agitation improves rinsing efficiency. Air agitation is simple, inexpensive and efficient for inducing agitation in a rinse tank (Figure 5). The system is comprised of an air distribution line and an air blower or compressor. Air is introduced through a perforated pipe into the bottom of a tank. A blower is preferred over a compressor because the latter may introduce oil vapors into the agitated tank. Moreover, a blower has advantages of lower energy consumption and capital cost.

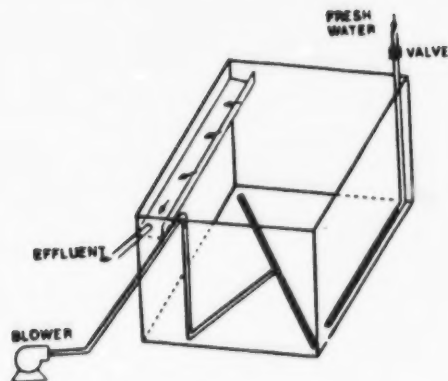


Figure 5 Air agitation system

Dragout Minimization

Figure 6 illustrates the definitions of dragout and drag-in, and the use of a drip board between a plating bath and a rinse tank. The drip board should be positioned at an angle to allow liquid to return to the plating bath. It may seem silly but we have been in a plant where the drip board sloped toward the rinse tank. Material for the drip board surface may be coated metal or plastic such as, polyvinylidene fluoride, polyvinyl chloride, polypropylene or polyethylene.

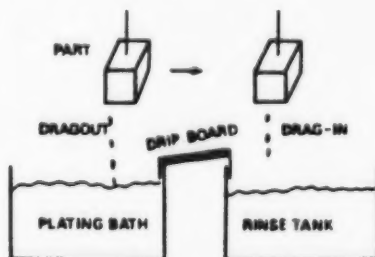


Figure 6 Dragout

There are several techniques which can be used to reduce dragout:

- . Use the lowest possible metal concentration of a plating solution. For example, a standard chrome bath is operated at 250 g/L (CrO_3). However, satisfactory results can be obtained at 150 g/L except for some critical or complex applications³. Dragout is reduced both in volume and concentration only at the expense of a longer plating time.
- . Tumble or rotate the parts (barrels) after withdrawal.
- . Drill out all of the barrel holes to return them to original size.
- . Proper design of racks for better drainage.
- . Use an adequate draining time. Care exercised by an operator is very important in reducing dragout. To help reduce operator's fatigue, install a hoist delay timer on a manual hoist line, or dwell hooks or slotted racks over tanks on a hand-line to provide the time delay needed for adequate draining. The optimum draining time can be determined by trial and error.

Drag-out Recovery (Dragout Tanks)

In the last section, various means to minimize dragout were discussed. However, a certain amount of process solution will still cling to parts, barrels or racks. Here, a simple, low-cost dragout tank for dragout recovery is introduced.

Dragout tanks are a series of still rinse tanks after a process tank. The workpieces are rinsed in these tanks before they enter a flowing rinse (Figure 7). It should be noted that a dragout tank may be positioned directly before or after a plating bath, depending on the availability of space.

Dragout tanks also serve the purpose of protecting the running rinse water. The more dragout tanks used, the lower the concentration of pollutants in the running rinse. Each dragout tank decreases, as a rule of thumb, the concentration in the running rinse by 50%.

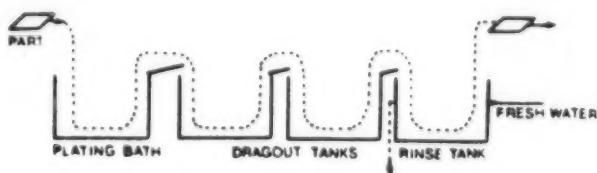


Figure 7 Dragout tanks

Operation of Dragout Tanks. The solution from the first still tank must be drained and replaced by the less contaminated solution from the second, and the second must be filled with deionized or distilled water.

The quality of water used to prepare bath solutions is of great importance in plating processes. Some impurities in tap water may harm finishing processes. Thus, if tap water or ground water is used to make up for evaporative losses, water impurities will become concentrated with time resulting in the need to more frequently dump bath solutions. The solution drained from the first dragout tank may be used to replace evaporative losses in the plating tank. For this reason, only de-ionized or distilled water is used to fill the second dragout tank. Moreover, this helps minimize problems of spots on dried plated parts resulting from dissolved solids.

Dragout tanks are best applied after a heated plating bath, such as nickel, hard chrome, copper and gold, allowing the dragout to be used for the replenishment of evaporative losses. It has been reported⁶ that 100% recovery of the dragout can be achieved in trivalent chromium plating processes.

Returning the dragout to the plating bath will not only recover the valuable raw chemicals, but also in turn minimize hazardous waste generation. Thus, it provides an income rather than a payout for environmental control.

Process Modifications/Operational Changes

Process modifications and operational changes include any major and minor redesign of manufacturing processes for the purpose of waste reduction. For example:

- . Install flow regulators.
- . Redesign racks to improve drainage.
- . Improve the rinsing efficiency by lifting the barrel momentarily out of the rinse tank, allowing it to drain and reimmersing it instead of being left immersed.
- . Use warm water rinse after an electro cleaning or alkaline-cleaning stage. It will help wash the soapy film off the part surface, thereby increasing the service life of the acid dip or pickling solution (Figure 2).
- . Increase the anode area and the bath temperature, if possible, to avoid the build up of trivalent chromium in a hexavalent chromium plating bath.
- . Reduce the build up of trivalent chromium in a hexavalent chromium plating bath by electrolysis using an extremely small cathode area. Knil and Chessin⁴ suggested a lead-anode-to-cathode area ratio of 30:1, and adequate agitation at 135-140°F, using a cathode current density of 3-5 A/in². This can be tried out over a weekend.

- . Use atmospheric evaporators where dragout volume is greater than evaporative losses.
- . Maintain bath heat at elevated temperature during non-normal operating hours to provide additional room (through evaporation) for dragout return. It involves no capital investment, but some increase in energy cost.
- . Use electrolytic strippers to replace chemical baths, thus eliminating chemical dumps.
- . Use water sealing instead of chemical sealing (e.g. sodium dichromate) for anodizing process.

Installation of Dragout Tanks. If space is not adequate, a small dragout tank may be hooked up to the front or rear end of a plating tank (Figure 8).

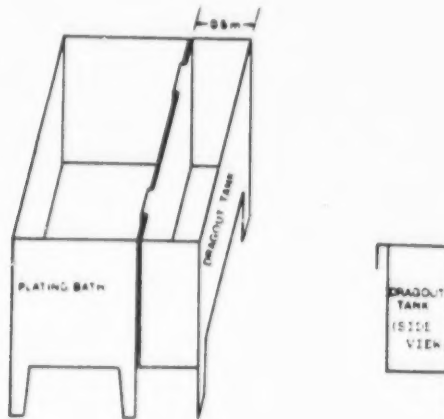


Figure 8 Installation of a small dragout tank

Use of Rinse Water as Bath Make-up Liquid. The use of rinse water as a make-up liquid for evaporative losses from a process tank can be considered as an extension of the counterflow rinsing concept described previously.

In hot galvanizing, the caustic rinse water which washes caustic off the workpiece can be fed back to the hot caustic tank to compensate for evaporative losses; fresh tap water is added only to the caustic rinse. The flow of feed back rinse is limited to the amount of evaporative losses in the hot caustic tank.

In the acid pickling step, the sulfuric acid rinse can be fed back to the hot sulfuric acid tank. If warm hydrochloric acid (70%) is used for pickling, only a small quantity of the acid rinse can be recycled back to the acid pickling tank in which little evaporation takes place.

Material Substitutions

Cyanide-Free Baths. Cadmium and zinc cyanide baths are costly, dangerous to operate, and expensive to treat. Their spent solutions are regulated under the Canada Transport of Dangerous Goods Act and various provincial and municipal regulations.

Cyanide-free processes for cadmium and zinc plating have been developed to replace cyanide baths. It has been the trend in the past decade to replace the cyanide zinc baths with non-cyanide zinc to avoid dealing with cyanide waste problems; the ratio is now better than 2:1 in favor of non-cyanide². This type of material substitutions will eliminate the need for alkaline chlorination for the treatment of cyanide. Thus, using cyanide-free baths will result in a net saving.

ASTM B-253 recommends two cyanide-free nickel strike baths for plating on aluminum, one operated at ambient temperature, and the other, at high temperature, while eliminating the cyanide copper strike. These solutions might also be used to plate nickel on zinc⁶, e.g., zinc die castings.

Zinc castings are normally plated successively with cyanide copper, electroless nickel and chromium to provide corrosive protection and a decorative appearance. A cyanide copper strike coating promotes good adhesion of the main deposit; without it, immersion coatings would be formed on zinc surfaces resulting in poor adhesion to zinc. Recent developments reportedly allow plating of nickel on zinc die castings while eliminating a cyanide copper strike^{1,7}.

Trivalent Chromium Baths. A trivalent chromium bath has the advantages, as compared to its hexavalent state bath, of reduced dragout volume due to its less concentrated bath solution; less sludge generated due to a lower metal content in the bath solution.

Non-Accelerated Amorphous Chromate Conversion System. Amorphous chromate conversion coatings are used by industry as pretreatments for organic finishes of aluminum and unpainted aluminum. They assist paint adhesion and promote corrosion protection. The chromate coating bath commonly contains ferricyanide, an accelerator, to enhance the coating formation rate. Recently the increasing concern for environmental pollution has led to the development of non-ferricyanide, non-accelerated, chromate conversion coating baths⁵.

Chrome free Conversion Coating Baths. The formulations used in this process may consist of any combination of titanium, zirconium, tannins, fluorides, phosphates and nickel compounds. They are now widely used as substitutes for chromate coatings on aluminum and its alloys to promote paint adhesion and corrosion resistance. A proprietary non-chromated conversion coating process⁹ claims that, in addition to eliminating chromium from the plating line, it also shortens the processing sequence by eliminating rinse tanks. The process consists of a non-etching cleaning tank, followed by a water rinse, then the conversion coating; no rinse need follow the coating treatment. Prior to painting, workpieces are warm air or oven dried. This chrome-free, dry-in-place coating produces no drag-out from the coating tank thereby eliminating the need of drag-out treatment and disposal.

Waste Exchange Opportunities

One company's waste may be another's raw material. For example, sulfuric and hydrochloric acids are commonly employed for removing oxide scale from steel and iron. The resulting spent pickling liquor may contain up to 7% free acid and 5% ferrous ion. It may be reused for the following purposes:

- . Coagulant in wastewater treatment
- . Phosphate control and sludge conditioning
- . Treatment of complexed and chelated copper rinse waters

Ferrous ion, when mixed with chelated copper, reduces Cu^{++} to Cu^+ at pH of 3 to 4; as the pH is raised to 9, Cu^+ is precipitated as CuOH .

In Ontario, one smelter is accepting dry metal sludge for extraction and recovery of high nickel or copper content.

Metal finishing plants should examine the possibility of this type of waste reuse by other industrial users. A good place to start is to contact the provincial or national waste exchanges.

Housekeeping Improvements

Basic good housekeeping practices are the most significant first step a company should take in reducing wastes.

Reduction of Spills and Leaks. Spills, tank overruns and leaks are common problems for metal finishing operations. Steps should be taken to reduce their frequency and impact, for example:

- . Train personnel in better handling and control of hazardous materials and wastes.
- . Prevent further occurrences of spills by analyzing their causes.
- . Fix leaks promptly.
- . Institute a preventative maintenance program.

Removal of Dropped Parts in Plating Baths. This can be done daily using a wooden or plastic coated rake, or a magnet for iron parts. Dropped parts contribute to heavy metal buildup in a bath. Removing parts dropped not only reduces the rejection rate of plated workpieces resulting from build-up of dissolved metal, but also extends a bath life. This, in turn, would reduce waste generation.

Removal of sediment from cleaner tanks and rinse tanks. Good housekeeping is a part of the answer for achieving quality cleaning and rinsing. It will also reduce the generation of waste water.

In addition to the above, there are other areas that may need attention such as inventory control and training of personnel.

CASE STUDY

Plant A is a medium-sized jobshop that operates three plating lines providing several types of metallic coating services utilizing 42 process and 28 rinse tanks:

- . Barrel line: zinc (CN-base), cadmium (CN-base) and tin plating
- . Rack line: zinc (CN-base), and cadmium (CN-base) plating
- . Hand line: cadmium (CN-base), copper, nickel, tin, silver (CN-base) plating; conversion coating on aluminum

The plant generates about 90 GPM of wastewater which is directly discharged into the municipal sewer system; spent solutions also drain to the city sewer system after pH adjustment.

The plant manager and owner appear to have limited knowledge of good waste management practices. Because of the growing concern about the new provincial regulations and a proposed City Sewer By-law to set limits on metal content, they have shown their desire to improve waste management at their plant.

Few, if any, simple techniques for waste reduction are employed in the plant. Most rinse water tanks used are of the single flow-through type. Although some process tanks use two-station counterflow systems, incomplete mixing of the rinse water is evident. No air agitation is incorporated in the rinse tanks and single-dragout tanks are used after some plating baths.

The plant utilizes a non-chromated conversion coating process for prepaint treatment of aluminum thereby eliminating the problem of chromium treatment and disposal.

A two-phased strategy has been recommended¹⁰ to improve waste management at the plant. Phase I comprises 24 recommendations, seven for the rack line, four for the hand line, and thirteen various others. These 24 recommendations should reduce the volume and toxicity of wastes through reuse of rinse water, air agitation, operational changes and process modifications, material substitutions and good housekeeping practices. Most of the recommendations could be implemented easily without the need for any sophisticated equipment. Preliminary data show that the waste volume may be reduced as much as 70% on the barrel and rack lines if Phase I-recommendations are implemented. It is estimated that the plant, after Phase I, would comply with the proposed city sewer by-law effluent limits, except for zinc concentrations.

SUMMARY AND CONCLUSION

A technical assistance program in waste reduction was initiated by Environment Canada's Western and Northern Region in the fall of 1986. It offers assistance in plant waste assessment and training on how to reduce waste. Four metal finishing plants have benefitted from the waste assessment component. To date, one training course which attracted 33 platers has been held on metal finishing waste management. The program demonstrates that government and industry can work together in a constructive way to solve waste management problems. Environment Canada also administers two financial incentive programs for pollution control and prevention.

There are various simple techniques that can be used to reduce waste at source. These simple techniques represent sound approaches for solving the waste disposal problems faced by the metal finishing industry as provincial regulations and municipal sewer use by-laws become more stringent.

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